NASA TECHNICAL NOTE

NASA TN D-6999

NASA TN D-6999

EFFECT OF NITROGEN ON TENSILE PROPERTIES AND STRUCTURES OF T-111 (TANTALUM - 8-PERCENT-TUNGSTEN - 2-PERCENT-HAFNIUM) TUBING

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1973

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TN D-6999		

4. Title and Subtitle	5. Report Date
EFFECT OF NITROGEN ON TENSILE PROPERTIES AND STRUCTURES OF T-111 (TANTALUM - 8-PERCENT-TUNGSTEN - 2-PERCENT-HAFNIUM) TUBING	March 1973
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Robert J. Buzzard and Robert R. Metroka	E-7285
	10. Work Unit No. 503-25

9. Performing Organization Name and Address	11. Contract or Grant No.
Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135	
	13. Type of Report and Period Covered: Technical Note

12. Sponsoring Agency Name and Address	14. Sponsoring Agency Code
National Aeronautics and Space Administration Washington, D.C. 20546	

15. Supplementary Notes

16. Abstract

This study involved an evaluation of the effect of controlled nitrogen additions on the mechanical properties of T-111 (Ta-8W-2Hf) fuel pin cladding material proposed for use in a lithium-cooled nuclear reactor concept. Additions of 80 to 1125 ppm nitrogen resulted in increased strengthening of T-111 tubular section test specimens at temperatures of 25° to 1200° C. Homogeneous distributions of up to 500 ppm nitrogen did not seriously decrease tensile ductility. Both single and two-phase microstructures, with hafnium nitride as the second phase, were evaluated in this study.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Metals Materials Nuclear reactors	Unclassified - unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	32	$3.00

* For sale by the National Technical Information Service, Springfield, Virginia 22151

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SUMMARY

The effect of nitrogen additions on the tensile properties of T-111 (Ta-8W-2Hf) tubing was investigated over a temperature range from room temperature to 1200° C. Nitrogen concentrations of 80 to 1125 ppm were added to the test specimens by heating them for times of 8 to 15 hours at about 1430° C in a nitrogen partial pressure of 0.1 newton per square meter (1×10^{-3} torr), followed by a homogenization anneal of 8 hours at 1430° C in a partial vacuum of 1×10^{-4} newton per square meter (1×10^{-6} torr). Nitrogen additions up to about 400 ppm resulted in a single-phase microstructure; higher concentrations usually resulted in a two-phase microstructure with hafnium nitride (HfN) as the second phase.

The tensile strength of the T-111 increased at all test temperature in proportion to the addition of nitrogen. The strength of T-111 containing nitrogen as a homogeneous solid-solution additive was proportional to the nitrogen content raised to the 0.17 power.

Homogeneous solid solution additions of about 450 ppm or less nitrogen to the T-111 tubing did not seriously affect either the tensile elongation values for specimens tested from room temperature through 1200° C or the ductility of rings sliced from the tubing and flattened at room temperature. However, increasingly severe embrittlement occurred in both tests at nitrogen levels above 500 ppm.

The results of this study are also discussed as they apply to the properties of T-111 cladding in nuclear reactor fuel pins. Sustained fuel pin temperatures as high as 1250° C in the vicinity of a cracked tungsten liner, with uranium mononitride (UN) as the fuel, should be feasible with no adverse effects of nitrogen transport on the tensile strength or the ductility of the T-111 cladding.

INTRODUCTION

A compact, liquid-metal-cooled, fast spectrum, space-power reactor concept is being studied at the NASA-Lewis Research Center (ref. 1). The reactor operating goals are 50 000 hours at a fuel pin cladding temperature of 980° C.

In this concept the tantalum base alloy T-111 (Ta-8W-2Hf) has been selected for intensive study as the fuel pin cladding material with uranium mononitride (UN) as the fuel and lithium as the coolant (ref. 2). A thin 0.013-centimeter (0.005-in.) tungsten liner will separate the cladding from the fuel to prevent direct contact and reaction between UN and T-111. However, since tungsten is a brittle material at low temperatures, it is possible that the tungsten liner could become cracked, either during fuel-element assembly or during reactor operation, due to thermal-cyclic induced strains. A cracked tungsten liner would then allow vapor-phase transport of thermally dissociated nitrogen from the UN to the T-111. As predicted by Gluyas (ref. 2), the rate of nitrogen increase in the T-111 would be affected primarily by the temperature of the UN. The maximum amount of nitrogen expected to be transported to the T-111 would be less than 1 ppm by weight at 1040° C, 5 ppm at 1140° C, 200 ppm at 1240° C, and 5000 ppm at 1340° C.

Since the reactor concept requires the fuel-element cladding to operate at 980° C with a maximum fuel temperature of about 1030° C, no problem of nitrogen transport should exist, should the liner develop a crack. However, should either local hot spots or temperature excursions occur or should the operating temperature of the reactor be intentionally increased to obtain greater efficiency (as discussed in ref. 3), it is imperative to know how the mechanical properties of the T-111 cladding would be affected by the possible higher nitrogen impurity level. The present study was undertaken to obtain such knowledge and to evaluate whether this pickup of nitrogen by the cladding could be detrimental to the operation of the fuel element.

In this study test specimens were machined from T-111 tubing and doped with nitrogen to levels ranging from 80 to 1125 ppm. Tensile tests were performed at temperatures ranging from room temperature to 1200° C. Ring-flattening tests served to determine the effect of nitrogen on the room-temperature ductility of the T-111. Microstructural analyses were performed by use of light microscopy and electron microscopy. Identification of precipitated particles was accomplished by X-ray and spectroscopic examination of particles extracted from the T-111.

EXPERIMENTAL METHODS

Material

The material used in this study was from a single lot of commercially produced, drawn-and-straightened, T-111 (Ta-8W-2Hf) tubing with an outside diameter of 1.9 centimeters (0.75 in.) and a wall thickness of 0.15 centimeter (0.060 in.). The tubing was annealed at 1650° C for 1 hour, followed by an anneal of 1315° C for 1 hour. The chemical analysis of this material is shown in table I. Duplicate analyses of machined speci-

TABLE I. - TYPICAL CHEMICAL ANALYSIS OF T-111 TUBING USED IN THIS STUDY

Major alloying elements,[a] wt.%			Other elements,[a] ppm by weight				
Ta	W	Hf	C	O	N	H	Zr
Bal	7.9	2.3	28	13	18	0.9	440

[a]Carbon content determined by combustion. Oxygen, nitrogen, and hydrogen determined by vacuum fusion. Remaining elements determined by wet chemistry.

mens were made periodically to insure that the material was homogeneous with regard to impurities.

Test Specimens

Tensile specimens were machined from this material before the doping operation. This was done by first slitting 7.6-centimeter (3-in.) sections of the tubing lengthwise into three equal segments and subsequently grinding and drilling the segments to obtain the configuration shown in figure 1. Two gage marks were scribed into the convex face of the specimens at a 2.5-centimeter (1-in.) interval.

Ring specimens measuring about 0.63 centimeter (0.25 in.) long were sliced from the tubing for use as flattening-test specimens and as experimental-doping specimens. The cut faces of these rings were wet-sanded with 400-grit polishing paper before doping, where flattening tests were involved. The original inside-diameter and outside-diameter surfaces of the test specimens were not altered in any way except where this

altering constituted a part of a specific test (i.e., in the case of intentionally removing surface material as part of a chemical analysis study to determine the depth of penetration of the nitrogen).

Equipment and Procedures

Nitrogen doping. - The following equipment and procedures were used in the nitrogen doping of the test specimens of this study.

All specimens were cleaned by ultrasonically vibrating them in a solution of detergent and water, followed by separate rinses in water, acetone, ethyl alcohol, and distilled water.

Doping was performed in an induction-heated vacuum furnace. The specimens were doped in groups of 10 per doping run to insure that the nitrogen content would be identical for all 10 specimens of a given test group. Also, this was the maximum number of specimens that could be conveniently accommodated in the furnace at any one time. The specimens were suspended into a cup-like tungsten holder, which in turn was placed within a larger tungsten cup that acted as a susceptor for the furnace. Because oxygen contamination of the specimens during doping had posed a serious problem at the beginning of this study, it became necessary to insert tantalum shielding between the two tungsten cups to act as a getter for this impurity. These shields were slit to allow a tortuous passage of the nitrogen to the specimens. New shields were prepared for each furnace run.

The susceptor and its contents were lowered into the heat zone of the furnace. The furnace was pumped down to its maximum attainable vacuum (about 3×10^{-5} N/m^2 (2×10^{-7} torr)), and then the specimens were heated slowly to the doping temperature. The doping temperature used in this study was about 1430° C. After stabilizing the temperature for about 30 minutes, high purity nitrogen gas (nominally 99.999 minimum vol.% N) was admitted to the furnace via a calibrated leak valve. With the diffusion pump still operating, the nitrogen partial pressure in the furnace was stabilized at about 0.1 newton per square meter (1×10^{-3} torr). Doping times of 8 to 15 hours were used in this study, resulting in nitrogen concentrations of 80 to 1125 ppm in the test specimens. There was no well-defined relation between doping times and resulting nitrogen concentrations in the specimens. But vacuum fusion analyses showed that all 10 specimens of a given group were doped to the same approximate level of nitrogen by this method.

After the doping was completed, the specimens were given a homogenization anneal in order to evenly distribute the nitrogen throughout each specimen. To do this, the nitrogen inlet valve was closed and the furnace was again allowed to pump down to the

maximum attainable vacuum. The furnace was run an additional 8 hours at the doping temperature.

In addition to the doping runs just discussed, a group of 10 tensile test specimens was given a 23-hour vacuum anneal at the doping temperature. This represented the longest total time at temperature that was experienced by any of the doped specimens. These 10 "simulated-doped" specimens were used to obtain baseline tensile test data in this study. The nitrogen content of these specimens was 14 ppm.

Although some insight into various methods of doping was obtained from the literature (e.g., refs. 4 to 9), it was necessary in this study to experimentally develop the doping parameters just discussed.

Evaluation of doping procedure. - The effectiveness of the doping procedure and homogenization anneal were evaluated by use of vacuum fusion analyses and microhardness measurements.

To check the effectiveness of doping and homogenization by chemical analyses, a doped-and-homogenized T-111 ring was sectioned into three pieces. One piece was analyzed by vacuum fusion analysis to determine the nitrogen, oxygen, and hydrogen levels resulting from the furnace procedure (to include surface chemistry); the other two pieces were surface ground on both the outside and inside diameters and subsequently were analyzed by vacuum fusion analyses. Variations in nitrogen distribution across the tube wall could thus be estimated by comparison of these analyses.

In order to further evaluate the doping and homogenization procedures, two T-111 rings were doped with nitrogen, and one of the two was given an additional 8-hour homogenization anneal at 1430° C in vacuum. Both rings were fractured in a brittle manner at room temperature in order to obtain segments for nitrogen analysis and for microhardness measurements. These microhardness measurements were taken as another means of estimating nitrogen distribution. Although a Knoop indenter with a 200-gram load resulted in the most satisfactory indentations for later use with the mounted-and-polished specimens of this study, a diamond pyramid indenter with a 500-gram load was more applicable for use on the unpolished surfaces of these fractured ring segments. And since hardness readings were to be taken both on the surface of the two rings and across their mounted and polished cross sections, the diamond pyramid indenter was chosen for this particular hardness survey.

Tensile testing. - After the doping and homogenization operations were completed, the tensile specimens were marked for identification, and pretest dimensional measurements were made. The initial gage length was determined by measuring the distance between two scribe marks located at a nominal 2.5-centimeter (1-in.) interval on the convex face of each specimen. The thickness and width of the gage section of each specimen were measured with a micrometer. Since the cross section of each specimen was in the form of a pie-shaped segment, the width was measured as a chord of the

outside diameter of the tube. And since calculation of area based on such measurements was tedious, a nomograph was developed for this purpose.

Tensile testing was performed by using a screw-driven tensile testing machine. The output of the load cell of the machine was fed into a strip chart recorder so that data were recorded as load versus time, the time axis being referred to crosshead movement rate. All testing was done at a crosshead movement of 0.13 centimeter per minute (0.05 in./min).

The testing furnace consisted of a stainless steel, O-ring sealed vacuum chamber with a double-walled, water-cooled shell. The system was capable of attaining vacuum on the order of 1×10^{-4} newton per square meter (1×10^{-6} torr); however, during specimen heatup, the pressure rose to about 1×10^{-3} newton per square meter (1×10^{-5} torr).

The specimens were radiantly heated using a resistance type of tungsten split-tube heating element powered by a variable transformer. Temperature was measured with a platinum/platinum - 13-percent rhodium thermocouple tied to the center of the specimen's gage length. The accuracy of temperature measurement was estimated to be about $\pm3^{\circ}$ C.

Special molybdenum tensile grips were fabricated for use in this program. The two-piece design shown in figure 2 was used because the curved surface, which positions the specimen properly for axial loading, could readily be ground eccentrically to a high degree of accuracy and parallelism with the load axis. Also, minor adjustments in specimen positioning due to variations in specimen thickness could be accommodated very easily with this design.

Posttest examination. - After tensile testing, the distance between gage marks was measured again for use in elongation calculations. The nature of the fractures was such that meaningful posttest measurements of cross-sectional areas could not be obtained for use in reduction in area measurements even though attempts were made both optically and with micrometers.

Part of the broken gage sections of selected specimens from each lot were submitted for microstructural observation and vacuum fusion analysis. The etchant used in the metallographic observations was a bifluoride swab etchant, consisting of a solution of 50 cubic centimeters nitric acid, 20 cubic centimeters water, and 30 grams of ammonium bifluoride.

The remains of one specimen from each group of 10 of a given nitrogen content was dissolved in a solution of 10 parts methanol and 1 part bromine, in order to extract any second-phase particles for X-ray and spectrographic analyses and for electron microscope observations. The methanol-bromine solution preferentially attacked the matrix material, thus freeing the particles.

Flattening tests. - In addition to the tensile testing just described, ring shaped specimens of nitrogen-doped T-111 were used to obtain an estimate of room temperature

ductility by means of a simple flattening test. The rings were placed between the crossheads of a hydraulically operated compression testing machine and deformed diametrically at a crosshead movement rate of 2.5 centimeters per minute (1 in./min). The rings were analyzed after testing to determine their exact nitrogen content.

RESULTS

Results of Doping and Homogenization

The typical interstitial contents of the nitrogen doped and homogenized T-111 used in this study, as determined by vacuum fusion analyses, are represented in table II. It appears from these results that the nitrogen was fairly evenly distributed throughout the T-111. The 815-ppm nitrogen content reported for the as-doped condition (analysis includes original surface material) remained essentially the same when thin surface layers were removed, which indicated that no heavily nitrided surface layer was present. After 30 percent of the surface material was removed, the nitrogen level remaining in the "core" of the ring dropped to 765 ppm, which is still within about 6 percent of the total original nitrogen content. Allowing for variability in analyses and piece-to-piece

TABLE II. - CHEMICAL ANALYSES OF NITROGEN-DOPED-AND HOMOGENIZED T-111 TUBING, SURFACE GROUND TO DETERMINE IMPURITY GRADIENT ACROSS WALL THICKNESS

Condition of material	Element,[a] ppm by weight		
	N	O	H
Undoped tubing (0.152 cm (0.060 in.) wall thickness)	14	39	0.7
Doped and homogenized (full wall thickness)	815	34	<0.5
Doped and homogenized (0.005 cm (0.002 in.) ground off inside and outside diameters)	816	24	1.5
Doped and homogenized (0.025 cm (0.010 in.) ground off inside and outside diameters)	765	24	2.9

[a]Determined by vacuum fusion analyses.

variations, this difference would not seem to be great enough to alter the results of this study.

The results of microhardness determinations as a method of estimating the nitrogen distribution in as-doped and doped-and-homogenized T-111 are shown in figure 3. The nitrogen contents of these specimens were 753 ppm for the as-doped specimen and 818 ppm for the similarly doped-and-homogenized specimen. The increased nitrogen content of the homogenized specimen may be partially due to variability in analysis but may also be a real increase because of the desorption of nitrogen from the furnace cups and shields and transfer of the desorbed gas to the specimen during the early stages of the homogenization run.

Reasons for the lower overall hardness of the homogenized specimen are not known, but this may be attributable to an overaging effect brought about by the longer time at temperature for this specimen. These results are comparable with the decrease in strength reported in reference 6 for the sister alloy T-222 (Ta-10W-2.5Hf-.01C) after aging between and 1315^{o} C or for strength decreases observed in T-111 doped with carbon and aged (as discussed in ref. 10).

Photomicrographs of the two specimens used in the microhardness tests are shown in figure 4. These were taken of the fracture zone after the specimens were purposely fractured in a room-temperature ring-flattening test. No great differences in microstructure between the two specimens was evident in regard to estimating the relative amounts of nitrogen, its distribution, or effects of the homogenization anneal. Both specimens show heavy precipitation within the grains. A clean-appearing zone outlines the grain boundaries of each specimen. Particles also appear to have been located within the grain boundaries, suggesting that these grain-boundary particles may have drawn on surrounding material for substance, resulting in the observed denuded zones. No further efforts were made to investigate the constitution of the various particles in the case of the ring specimens; however, the results of such investigation will be discussed later in regard to tensile specimens.

Hardness indentations can be observed in both specimens. In cases where cracks branched out into the material from the main transgranular crack (fig. 4(b)), hardness indentations were used to determine whether further crack propagation could be induced. This could not be accomplished using the 500-gram load and the diamond pyramid indenter.

An estimate of the room-temperature ductility of nitrogen doped and doped-and-homogenized T-111 was obtained by the use of ring-flattening tests. The flattening test results are plotted in figure 5. These results show that doped-and-homogenized T-111 tubing rings containing as high as 440 ppm nitrogen could be completely flattened with no evidence of cracking as represented by the "100-percent flattened" level on the figure. As the nitrogen content was increased beyond this level, the ability of the rings

to withstand such deformation decreased progressively until at about 900 ppm the rings immediately snapped apart as the load was applied.

As the figure indicates the flattening test results also included data for two T-111 rings that were doped with nitrogen but were not given the homogenization anneal. These rings had about the same degree of ductility as doped-and-homogenized rings with about the same nitrogen content, considering the data-scatter observed.

Tensile Test Results

Tensile test specimens also were doped with nitrogen and homogenized in the manner described previously. The microstructural effects of this doping are summarized in table III. The table indicates the nitrogen content, grain size, and type of microstructure observed for each treatment. It appears from these results that the addition of large amounts of nitrogen (440 ppm and above) resulted in a stabilization of grain size. Also, the higher nitrogen levels caused precipitation of a second-phase constituent (as will be discussed later).

Tensile test results for the specimens run in this program are shown in figure 6. The change in slope of most of the ultimate strength curves at intermediate test temperatures (650° to 800° C) was expected since T-111 is known to exhibit a strain-aging

TABLE III. - RESULTS OF NITROGEN DOPING[a] AND HOMOGENIZATION ANNEALING[b] OF T-111 TENSILE TEST SPECIMENS

Average nitrogen content, ppm	Type of microstructure	Average grain size, cm
[c]14	Single phase	0.0132
80	Single phase	.0094
440	Two phase	.0069
505	Single phase	.0074
740	Two phase	.0081
1125	Two phase	.0076

[a]Nitrogen doping was accomplished at 1430° C at a nitrogen partial pressure of ~0.1 N/m^2 (1×10^{-3} torr) for 8 to 15 hr.

[b]All specimens were homogenized at 1430° C in a partial vacuum of 1×10^{-4} N/m^2 (1×10^{-6} torr) for 8 hr.

[c]"Simulated doped" in vacuum at 1430° C for 23 hours (base-line data for comparison).

phenomenon (as reported in ref. 11 for T-111 sheet). In the referenced study strain-aging behavior in T-111 sheet was attributed to a complex atmosphere-dislocation interaction, wherein oxygen is the critical interstitial species responsible for this behavior. This was also probably the case for the T-111 tubing tested in the present study, with nitrogen also contributing to this effect. Strain aging was also characterized in this study by the occurrence of serrated stress-strain curves at the temperatures of the strain-aging peak.

As the nitrogen level was increased for the various lots of test specimens, the tensile strength also increased. The strain-aging peak was retained through all but the highest level of nitrogen studied (i.e., 1125 ppm, average). The temperature at which the peak strain-aging-affected strength occurred decreased from about 900° to about 760° C at nitrogen levels of 440 ppm and above.

The ductility of the tensile specimens may be assessed by observation of specimen elongation as a function of test temperature and nitrogen content (fig. 6). The elongation of the simulated-doped material (14 ppm nitrogen) and the material containing 80 ppm nitrogen remained at a constant value of about 30 percent from room temperature up to 760° C, after which it gradually decreased to about 12 to 15 percent at 1200° C. The specimens containing 440 and 505 ppm nitrogen followed the same trend, except that their low-temperature elongations were on the order of 20 to 25 percent. The materials containing the greatest amounts of nitrogen (740 ppm and 1125 ppm) were so brittle in tension at room temperature that failures of the test specimens outside the gage section precluded obtaining meaningful tensile test data at room temperature. These materials exhibited measureable elongation above approximately 400° C. The elongation of these materials reached a peak value of about 20 percent at 650° and 1000° C, respectively, and decreased again with temperature to about 10 percent at 1200° C (2200° F).

The 0.2-percent offset yield strength as a function of temperature is plotted in figure 6. This property also increased as the nitrogen content of the T-111 increased. The effects of strain-aging were also observed, but they were not as pronounced as in the ultimate strength curves. However, a definite strain-aging peak was apparent in the yield strength of the specimens with 1125 ppm nitrogen, although no similar effects were observed in the ultimate strength curve for this material. The reason for this anomaly is not known.

A cross-plot of the ultimate tensile strength data of figure 6 is shown in figure 7(a)). Generally, it can be seen that increased nitrogen content in the specimens resulted in an increase in tensile strength at all test temperatures investigated. Also, the isotherms could be separated into two parts, representing single-phase and two-phase microstructures. At all but the highest testing temperature, the single-phase structure resulted in greater strengthening with increasing nitrogen content than was the case for the two-

phase structure. In effect, the solid solution strengthening mechanism was more effective than the precipitation, or dispersed-phase, mechanism.

By replotting these data on log-log coordinates (see fig. 7(b)), it was readily apparent that, for single-phase material, the increase in strength was proportional to some power of the nitrogen content at all test temperatures studied. The average proportionality constant for this relation was determined as 0.17 (ranging from 0.155 to 0.172); that is, the slopes of the isotherms of this figure average 0.17.

Microhardness Results

Microhardness traverses taken across the thickness direction of the specimens in the failed gage sections are plotted in figure 8(a). The hardness impressions included both phases in the case of two-phase material. The readings were taken at areas far removed from the worked structure of the fracture zone so that the values would not be affected by the previous tensile testing. It can be seen that the hardness was quite uniform across the thickness of the specimens. Also, traverses taken along the gage length (not shown) of several of the specimens indicated uniformity. Interpreted as an indication of nitrogen distribution, these results would indicate that the nitrogen distribution was fairly homogeneous throughout the test specimens.

The average value of each hardness traverse is shown along the ordinate of figure 8(a). These average values are plotted as a function of nitrogen content in figure 8(b) in order to more clearly indicate the relation among hardness, nitrogen content, and microstructure. As with the tensile data, the hardness data can be separated by observed microstructure. Also, the figure indicates that for comparable nitrogen levels (about 500 ppm) the hardness of the T-111 is more strongly influenced by nitrogen in solid solution than by nitrogen as a second-phase constituent. Similar observations were made by Stoop and Shahinian (ref. 5); however, the occurrence of two microstructures at the same general nitrogen content in this study allows a close comparison of this type to be made over a more limited range of nitrogen contents (e.g., 14 to 1125 ppm for this study) as compared with the wider range of nitrogen contents of Stoop and Shahinian's study (45 to 4600 ppm).

Microstructure

The gage sections of selected tensile-test specimens were examined metallographically. Representative photomicrographs of some of these specimens are shown in figures 9 and 10.

Figure 9 indicates that the failure mode for all of the specimens tensile tested in this study was transgranular. Transgranular cracks were frequently observed extending into the specimens containing nitrogen levels of 440 ppm and greater. The cause of such cracking is not known, but the cracks may be a result of stresses arising from a probable tendency for the tube-section specimens to flatten in the gage section during tensile testing.

Microscopic examination of these specimens also indicated that, for tensile test specimens containing 14 to 505 ppm nitrogen, the grains appeared to be clean but the grain boundaries in the fracture zones contained large amounts of voids (see fig. 10(a)). At the higher nitrogen levels (fig. 10(b)) the grain boundaries had smaller voids, but the grains contained a great deal of second-phase material (or voids resulting from metallographic preparation).

An exception to this observation is the series of specimens that contained an average nitrogen content of 440 ppm. These specimens contained a greater amount of intragranular second-phase material than the specimens containing the next higher level of nitrogen. These specimens were doped as described previously. However, at the completion of the doping run, the furnace was cooled to room temperature, and a spare sample was removed for a check chemical analysis. The tantalum gettering-shields also were removed in order to preclude the possibility of further transport of nitrogen to the specimens from the shields during the subsequent homogenization anneal. As a result, the homogenization temperature and cooling rate of the specimens after the anneal were probably not identical to those of the other homogenization runs of this study. In addition to the cool-down after doping, this change in the conditions of the homogenization anneal could have been sufficient to cause the second-phase structuring, or precipitation, observed at this nitrogen level. The next higher level of nitrogen at which such precipitation or second-phase structuring occurred was at the 740 ppm level of this study.

Second-Phase Identification

Further insight into second-phase identification and morphology was achieved by examination of test specimens with the scanning electron microscope (SEM) with energy dispersive analyses and by use of the electron microscope using replication and X-ray diffraction techniques. Two specimen preparation tehcniques were used in order to examine the precipitates with the electron microscope. One was that of fracturing the specimens at room temperature and examining the fracture surfaces, and the other was that of milling away the matrix material by an anodic etching technique.

A fractured surface of a 1200° C tensile test specimen containing 1150 ppm nitrogen was examined using scanning electron microscopy. Although the entire fracture surface of the specimen was scanned, there were very few areas in which particles could be seen. One such area is shown in figure 11. Since the specimen fractured transgranularly and in a brittle manner, the fracture surface was composed of cross sections of grains as opposed to grain boundary surfaces. It is probable, however, that grain boundary separations caused by previous tensile testing (as shown in fig. 11(a)) just below the center of the photograph) could result in the exposure of an intact grain boundary surface when the specimen was fractured at room temperature. (In fact, Stiegler (ref. 12) used high-temperature creep testing as a method of initiating grain-boundary separation, so that subsequent room-temperature fracturing of the specimens would provide exposed grain-boundary surfaces for transmission electron microscopy.) It is thought that the area shown in the upper central portion figure 11(a) and enlarged in figure 11(b) may be such an exposed grain-boundary surface. The direction of fracture of the main grain appears to have changed in this area. The matrix appears different from the surrounding material, and the material around the particles appears to have been deformed, which could be evidence of grain boundary sliding.

The white spots on the particles shown in figure 11(b) are areas where the electron beam was concentrated for energy-dispersion analysis. The dark area in the lower right corner of this photograph is a raster scan area where the composition of the matrix was determined over a wide area. Results of these analyses showed the ratio of tungsten, tantalum, and hafnium in the matrix to be similar to that of numerous previous scans of this type on T-111 (fig. 11(c)). However, the second-phase particles showed a vary high hafnium peak (fig. 11(d)) accompanied by a decrease in the tantalum and tungsten peaks. This indicates that the particles are composed primarily of hafnium with some tantalum and tungsten present; however, this analytical method did not determine whether the metals were combined as nitrides, oxides, etc.

Scanning electron microscope scans also were attempted for other specimens having lower nitrogen contents. But the lower nitrogen contents afforded some ductility to the material, and the cleavage surfaces were so amorphous in nature that attempts at locating particles were fruitless.

Further examinations of several test specimens were performed using an electron microscope in order to more accurately define the morphology and distribution of the second-phase particles. Preparation of polished specimens by the anodic etching technique resulted in good retention of the particles both in the grains and in the grain boundaries. Carbon replicas of the anodically etched surfaces were prepared for examination.

Examination of the replicated surface of a specimen containing 439 ppm nitrogen after tensile testing at 760° C revealed the presence of large amounts of particles both in the grains and in the grain boundaries (fig. 12). Since the particles have the same distribution in each grain, they are assumed to be of the same composition and origin but different in appearance because of the direction of observation.

In contrast to these observations, the specimen that was subjected to a simulated-doping treatment and tested at 760° C had a much cleaner appearing microstructure when its replica was examined with the electron microscope. The photograph of figure 13 shows a typical grain boundary containing very few particles.

Observations such as these verify the existence of actual second-phase particles in the material. This existence could only be implied when light metallography and its associated specimen preparation techniques were used. This verification supports the assumptions or conclusions that were made in this report regarding the effect of a second-phase structure on tensile properties or the microhardness of the material.

Further attempts to determine the composition of the particles in the T-111 of this study were made using X-ray analyses of the extracted particles. From these analyses it was determined that the particles in the highly doped T-111 were essentially hafnium nitride (HfN) with a slightly lower lattice spacing than the ASTM standard. This indicates that another element or elements may be alloyed with the hafnium. No discrete traces of tantalum nitride (TaN) particles were found. However, in such analyses very minute concentrations of TaN could remain undetected or could be masked by other more dominant diffraction lines.

Analyses of extracted particles also were performed using transmission electron diffraction with the electron microscope. These analyses also show the platelets observed in the high-nitrogen-containing T-111 to be HfN, but in the case of the simulated-doped material, only tungsten trioxide (WO_3) was identified. No evidence of hafnium oxide (HfO_2) was found.

In addition to these analyses extracted particles were spectrographically analyzed using the technique described in reference 13. The results indicated that the particles extracted from specimens with a two-phase microstructure were higher in hafnium than were particles extracted from specimens which had no intragranular precipitate or second-phase structure, but which did contain some grain boundary particles. The second-phase material's particles were composed of about 23 to 40 percent hafnium, as opposed to one to 2-percent hafnium in the particles extracted from the specimens which had only grain boundary precipitates. The remaining metals in the particles were tantalum and tungsten. These results corroborated the findings of the previously discussed analytical methods in identifying the metallic portion of the second-phase particles as an alloy of predominantly hafnium with tantalum and tungsten as minor alloying elements.

DISCUSSION

Application to Reactor Operation

The prime purpose of this study was to evaluate the effect of nitrogen on the mechanical properties of T-111 cladding material in nuclear reactor fuel pins. The nitrogen could originate by dissociation of the UN fuel and could be transported as a vapor phase into the T-111 should a crack occur in the tungsten liner that separates the fuel from the cladding. In addition to evaluating the effect of such nitrogen transport on the mechanical properties of the cladding at normal reactor operating temperatures, the effects of unintentional hot spots or temperature excursions should also be considered, as should the potential of intentionally increasing the reactor's operating temperature to gain further efficiency. The following discussion is addressed to relating the results of this study to such reactor needs.

At a reactor operating temperature of 980° C, less than 1 ppm of nitrogen would be expected to be transported into the T-111 cladding in the reactor's proposed 50 000-hour lifetime, assuming that the tungsten liner cracked at the beginning of reactor operation. This amount of nitrogen would not cause a noticeable change in the properties of the T-111 and should allow a margin of safety for temperature excursions or hot spots. Based on the strength and ductility results of this study and excluding effects of irradiation, proposed fuel pin operating temperatures as high as about 1200° C should be feasible (both fuel and cladding assumed to be at the same temperature) with some allowance for temperature excursions and hot spots to occur. At an operating temperature of 1200° C, calculations indicate that less than 100 ppm nitrogen would be transported into the T-111 during the 50 000 hours of reactor operation (ref. 2). This should cause no appreciable embrittlement of the T-111 cladding and might even increase the tensile strength of the cladding by about 40 percent at that operating temperature.

In fact, 50 000-hour operation at temperatures as high as 1250° C could possibly be realized with no degradation of the strength or the ductility of the T-111 resulting from nitrogen transport. For this time calculations (ref. 2) indicate that the nitrogen content would be about 300 ppm in the T-111 cladding material. The effect of 300-ppm nitrogen on mechanical properties, based on this study, would be to increase the tensile strength both at room temperature and at operating temperature by about 50 percent as estimated by extrapolation of the strength versus temperature plots of this study. The effect on tensile ductility, based on elongation data, would be a slight decrease at all temperatures, but the T-111 would still be capable of severe deformation even at room temperature.

Intentional operation of a reactor fuel element at 1250° C would not allow much margin for temperature excursions or hot spots, however. For example, an increase of only 50°, to 1300° C for 50 000 hours, could result in a maximum of about 1000 ppm

nitrogen in the T-111 cladding, as nitrogen transport increases exponentially with temperature. Although the T-111 would be still stronger than before, its ductility at the operating temperature would decrease still more (to about 8 percent). And equally important, this property would also decrease with decreasing temperature below about 600° C to essentially zero at about 300° C. This could cause the T-111 cladding to crack, should complex strains be imposed on the cladding, for example, as a result of temperature gradients during reactor cool down.

Not considered in this discussion are the roles of irradiation effects on the mechanical properties of the T-111 in addition to the effects of nitrogen additions and the effects of nitrogen additions on the creep properties of T-111 tubing. Both of these effects are worthy of further study before increased operating temperatures can be considered or before the full impact of fuel pin hot spots or reactor temperature excursions can be evaluated.

Applicability to Alloy Modification

The original goal of this study was to determine the tensile properties of the T-111 cladding of a nuclear reactor fuel pin after an unscheduled exposure of the pin to nitrogen transport from the uranium mononitride fuel. However, the knowledge gained from this work can also be applied to the upgrading of the alloy by the intentional addition of evenly distributed controlled amounts of nitrogen. For example, homogeneous additions of about 300 ppm nitrogen can result in an increase in tensile strength of about 50 percent at room or higher temperatures (at least up to 1200° C), while still maintaining usable amounts of ductility in the material. Similar results have been reported in the literature (refs. 6 to 9) where the primary goals have been tantalum (or tungsten) alloy development using nitrogen additions to achieve strengthening.

The addition of nitrogen to an alloy such as T-111 does indeed provide an attractive alloy modification. But T-111 type of alloys that contain nitrogen are susceptible to overaging; therefore, the limitations of this method of strengthening should be understood before such alloy modification is attempted. For example, the work of reference 7 includes creep test results for a nitrided tantalum alloy showing a significant improvement in this property at 1090° C as a result of the nitrogen addition. However, this advantage was decreased greatly when the material was held at a higher temperature for a time long enough to cause overaging of the nitrides (in this case, by creep testing at 1315° C for 300 hr).

Thus, for applications involving improved short-term tensile strength or, perhaps, even short-term creep resistance in T-111 at about 1200° C, small amounts of homogeneously distributed nitrogen added to the material would probably serve this purpose

quite well. However, should the material be exposed to higher temperature usage or to very long-term use at 1200° C, the possibility of a reduction in the strength advantage could result.

SUMMARY OF RESULTS

The following results have been drawn from this study, based on tensile tests from room temperature to 1200° C, room-temperature ductility and microhardness measurements, light and electron microscopy, and analyses of nitrogen-doped T-111 tubing of a size suitable for use as nuclear reactor fuel pin cladding material (i.e., 1.90-cm (0.75-in.) outside diameter and 0.15-cm (0.060-in.) wall thickness):

1. Nuclear reactor fuel pins having tungsten-lined T-111 as cladding and uranium mononitride (UN) as fuel should be capable of operating at temperatures as high as 1250° C in the vicinity of a cracked liner, with no adverse effects of nitrogen transport on the tensile strength or the ductility of the T-111 cladding.

2. Concentrations of 14 to 1125 ppm nitrogen in T-111 tubing resulted in an increase in ultimate tensile strength that was proportional to the nitrogen content in single-phase material at all test temperatures studied.

3. Homogeneous additions of 450 ppm or less of nitrogen to T-111 tubing did not significantly affect either the tensile elongation values (measured from room temperature to 1200° C) or the room-temperature ductility of rings sliced from the tubing (measured by flattening the rings). Severe embrittlement, however, occurred in both cases at nitrogen levels above 500 ppm.

4. A second-phase (precipitation) structure, which was observed in this study at nitrogen levels of about 440 ppm and greater was identified as thin platelets of predominantly hafnium nitride (HfN) with the hafnium being in solid solution with an alloying element or elements, most likely tantalum or tungsten.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 19, 1973
503-25.

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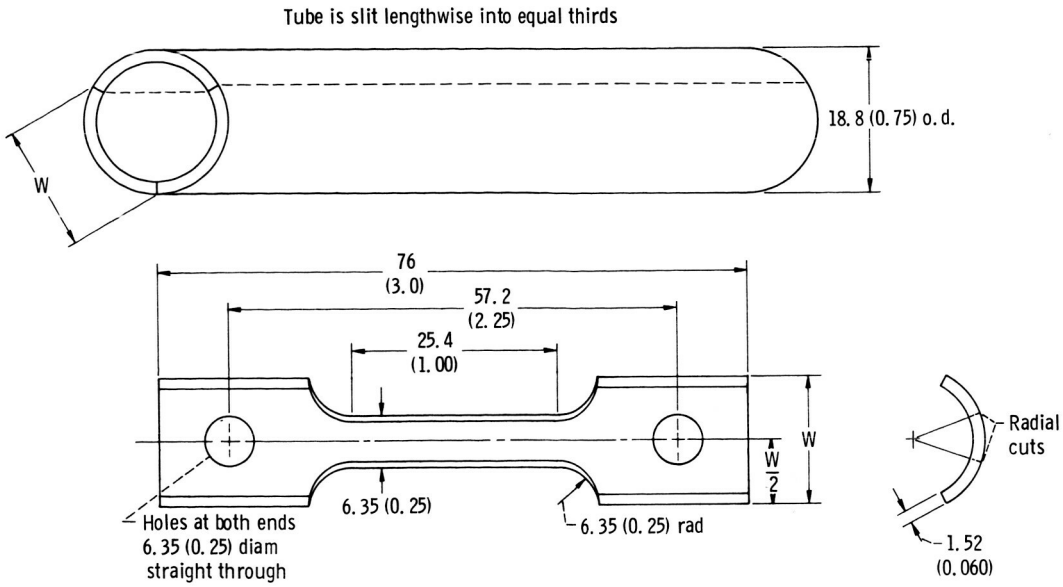

Figure 1. - Tube-section tensile test specimen. (Dimensions are in mm (in.).)

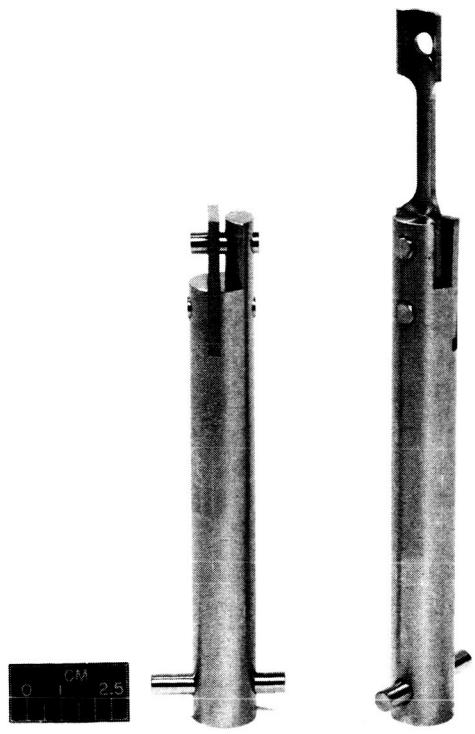

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Figure 2. - Tubing-section tensile-test specimen and grips used to test nitrogen-doped T-111 tubing.

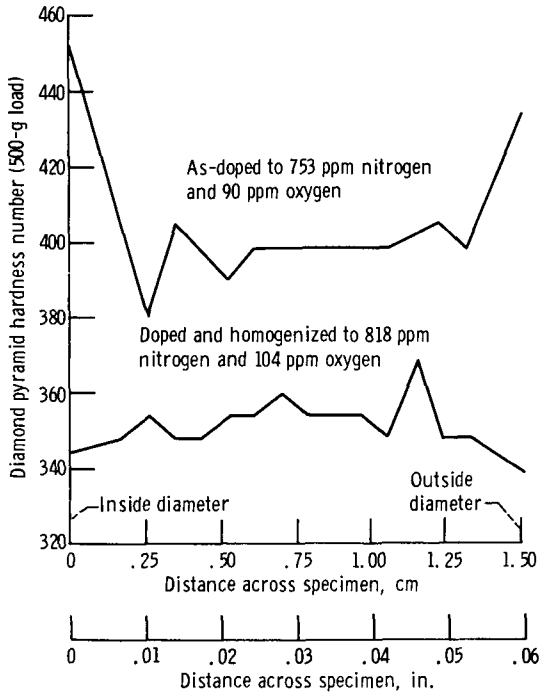
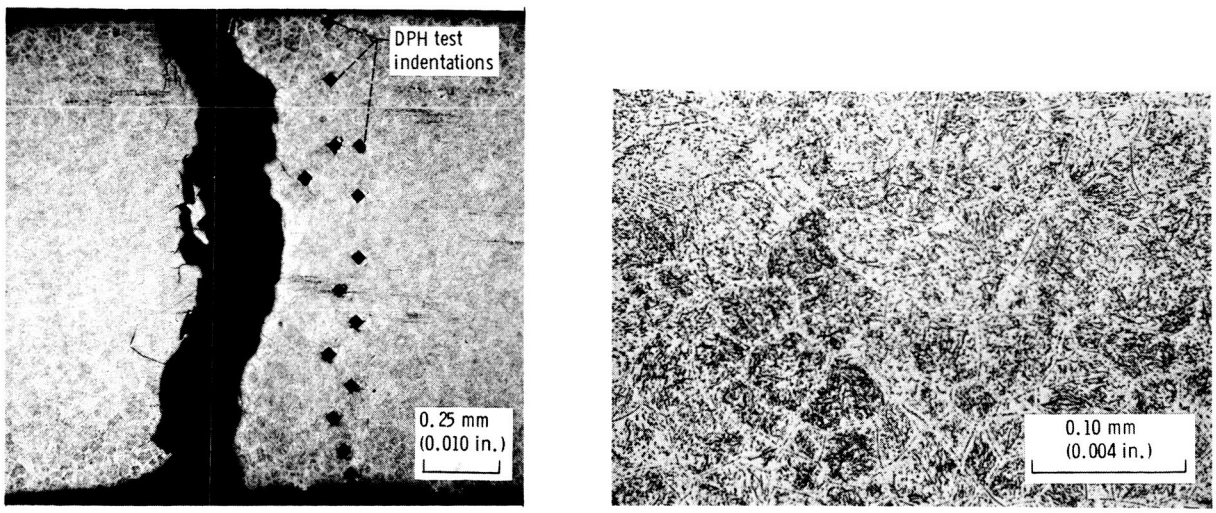
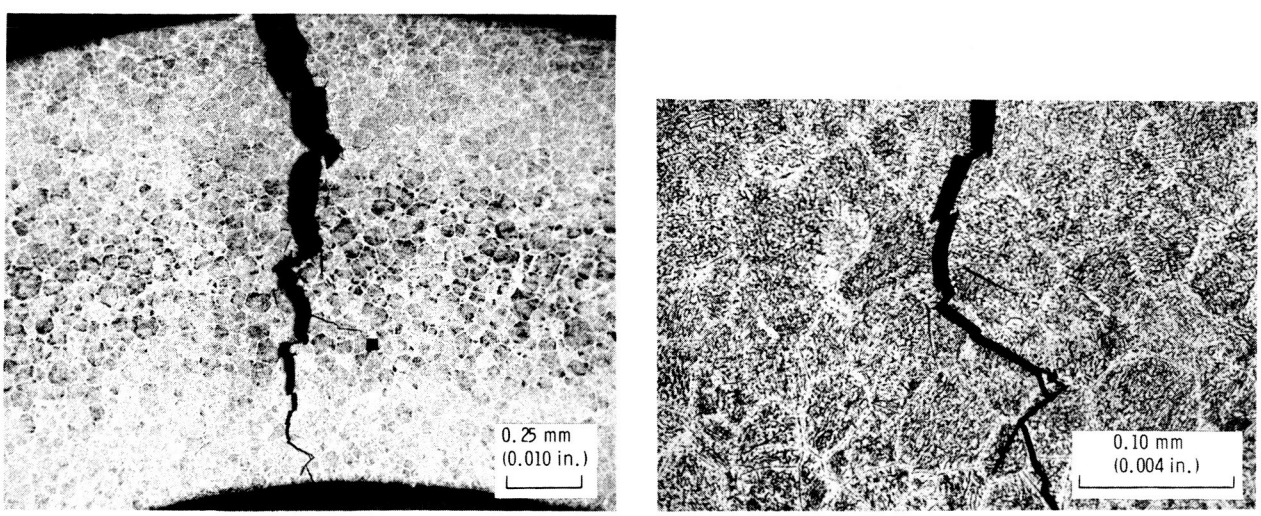


Figure 3. - Microhardness traverses across wall thickness of T-111 tubing, as-doped with nitrogen and after homogenizing at 1430^{0} C for 1 hour in vacuum.



(a) As-doped; 753 ppm nitrogen.



(b) Doped and homogenized; 818 ppm nitrogen.

Figure 4. - Photomicrographs of nitrogen-doped T-111 rings (after fracturing at room temperature and microhardness testing). Etchant: 50 cubic centimeters nitric acid, 20 cubic centimeters water, 30 grams ammonium bifluoride.

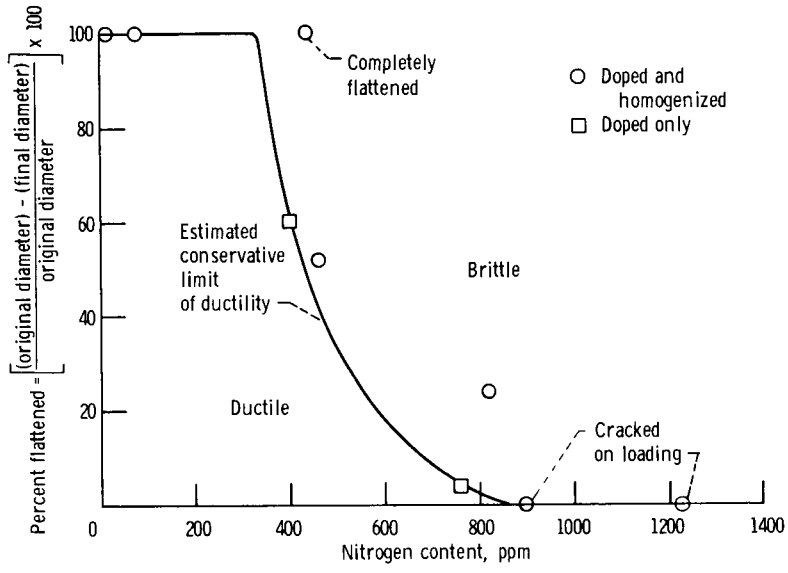


Figure 5. - Effect of nitrogen content on room temperature ductility of T-111 tubing as measured by flattening tests. Flattening rate, 2.54 centimeter per minute (1 in./min).

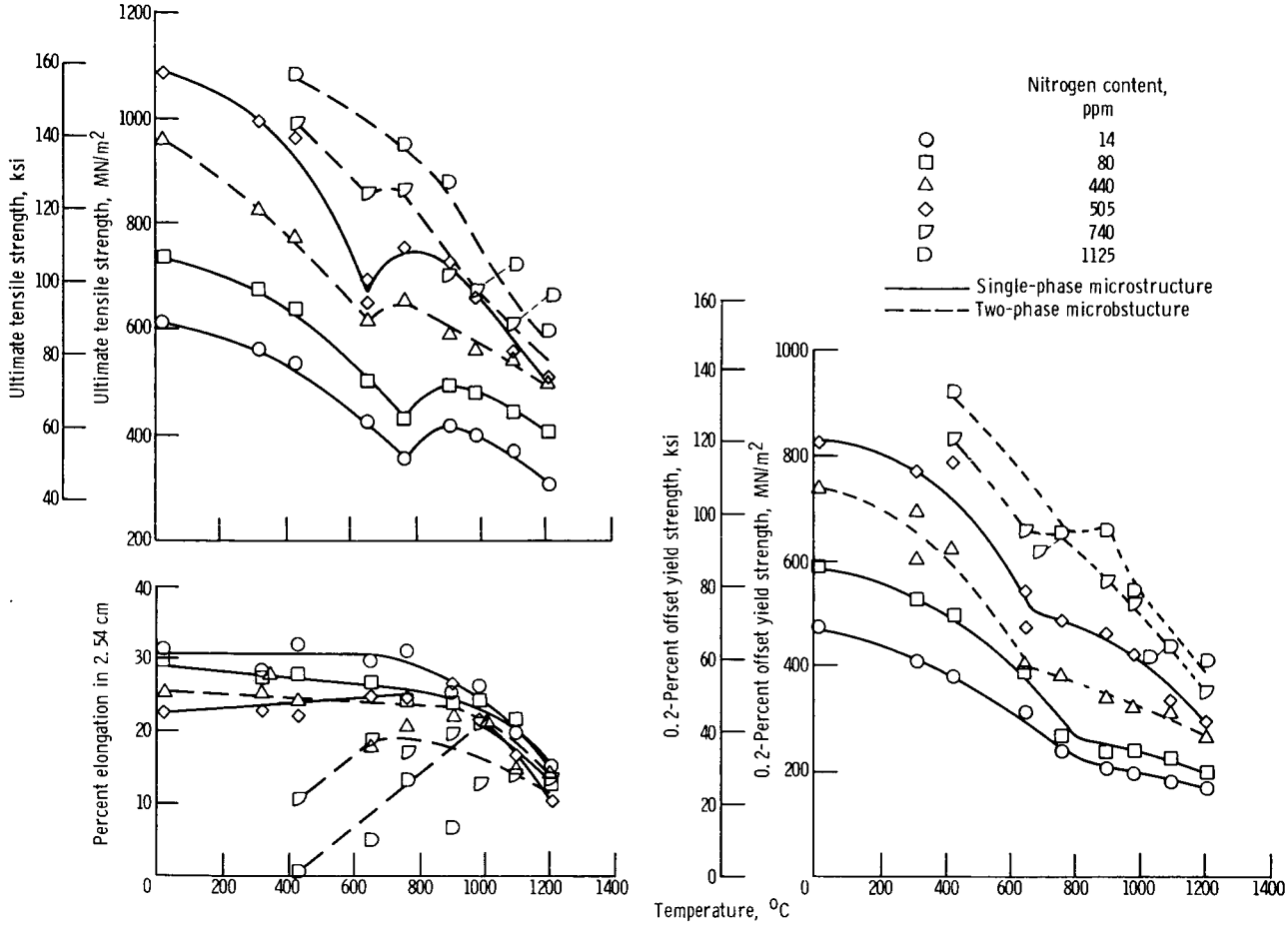
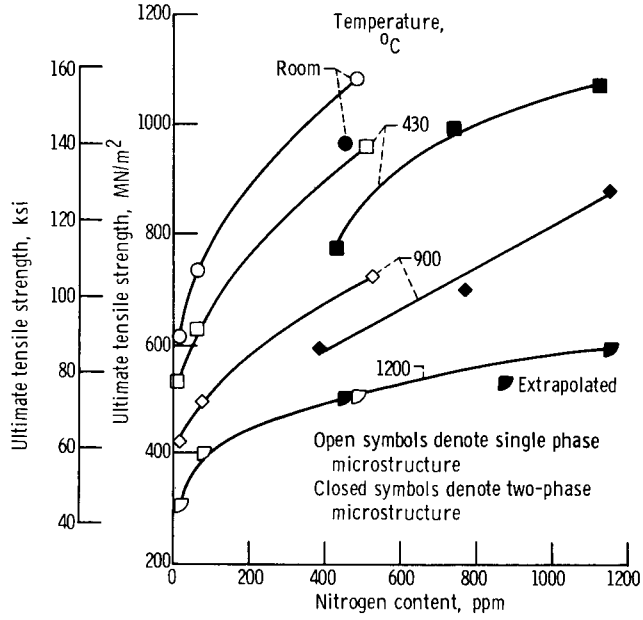
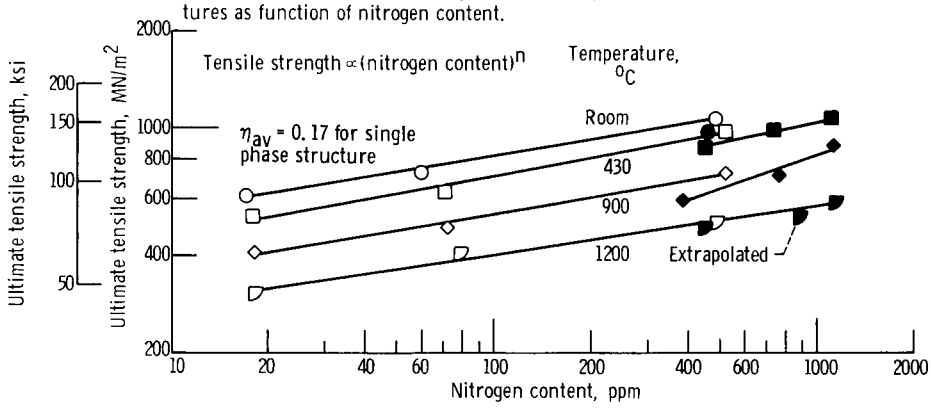


Figure 6. - Effect of nitrogen content on tensile properties of T-111 tubing.

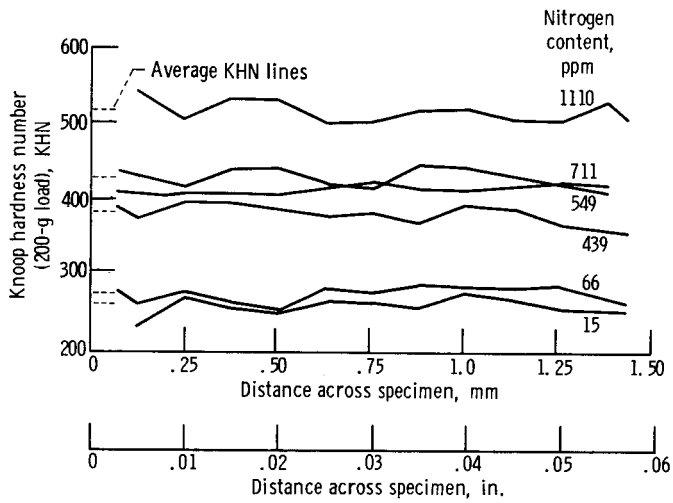


(a) Tensile strength of T-111 tubing at various temperatures as function of nitrogen content.

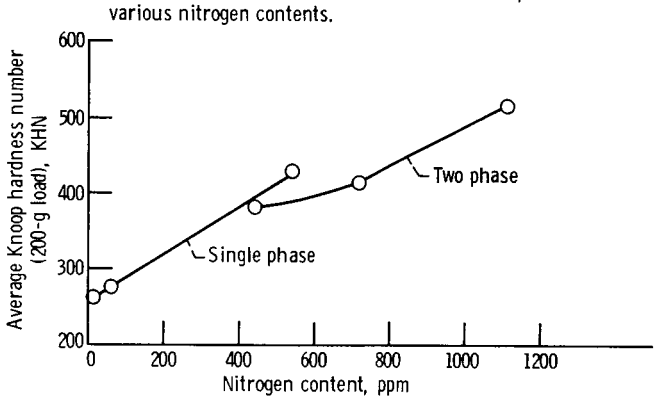


(b) Nitrogen dependence of tensile strength of nitrogen-doped T-111 tubing tested at various temperatures.

Figure 7. - Effect of nitrogen content and microstructure on tensile strength of T-111 tubing at various temperatures.

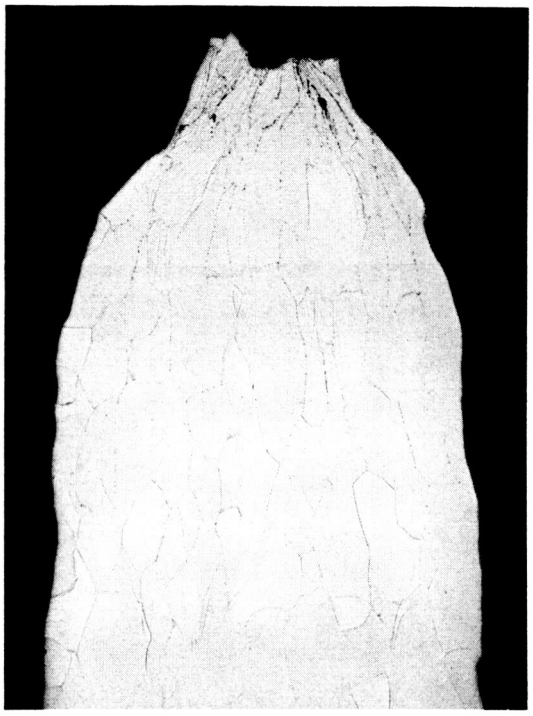


(a) Hardness traverses across thickness of T-111 specimens with various nitrogen contents.

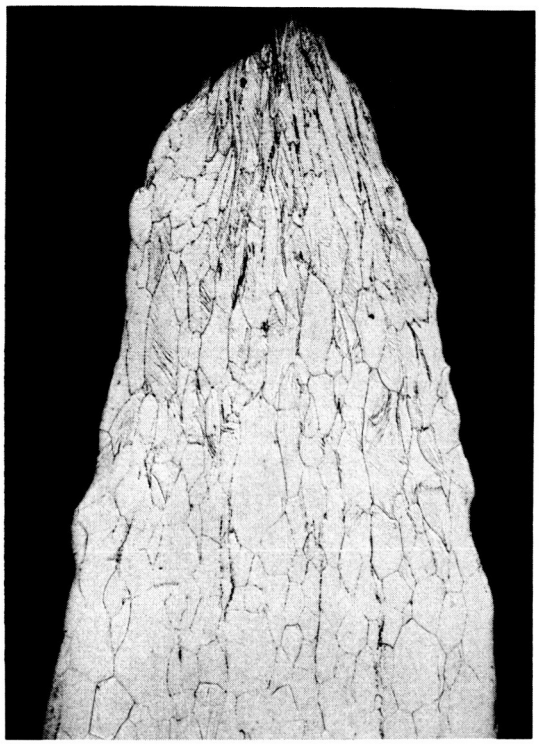


(b) Average hardness of T-111 tubing specimens as function of nitrogen content and microstructure.

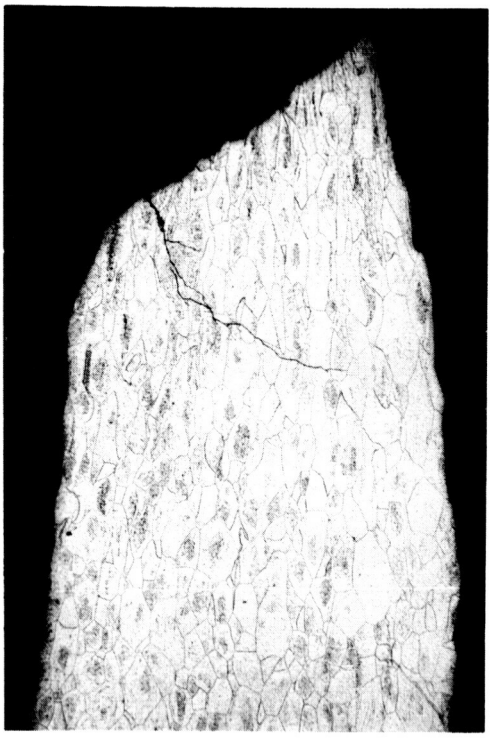
Figure 8. - Effect of nitrogen content and microstructure on microhardness of T-111 tubing tensile specimens tested at 760° C.



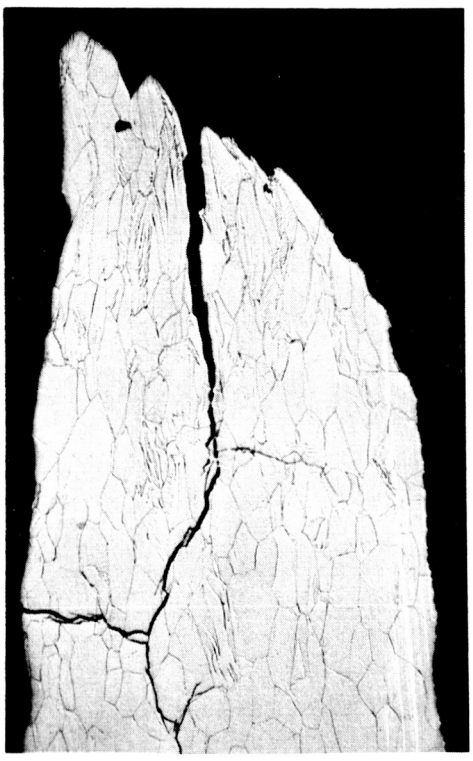
(a) 14 ppm nitrogen.



(b) 80 ppm nitrogen.

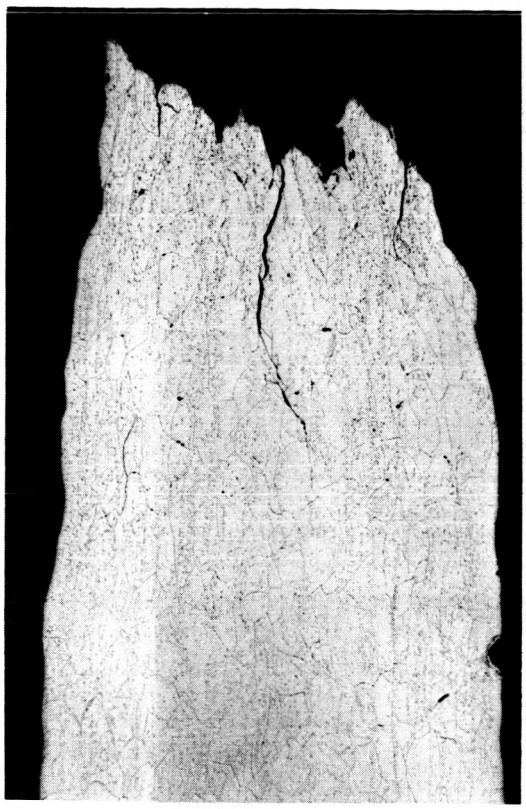


(c) 440 ppm nitrogen.

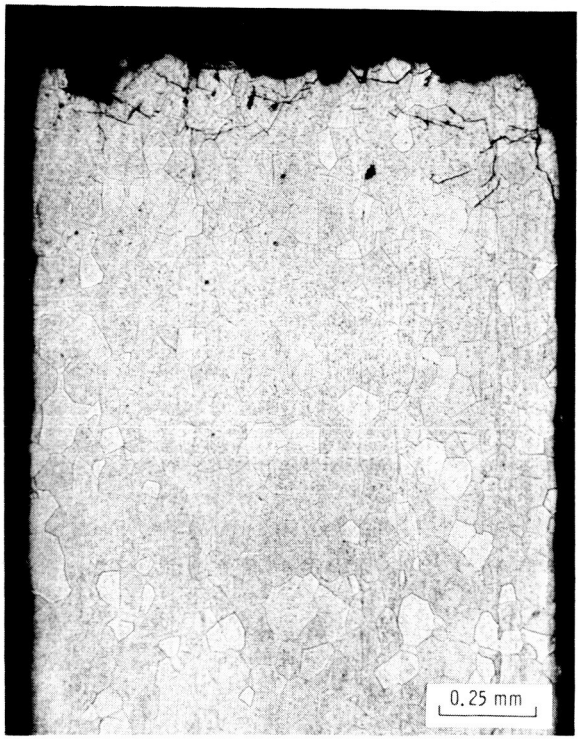


(d) 505 ppm nitrogen.

Figure 9. - Microstructures of test sections of T-111 tubing tensile specimens tested at 900° C. Etchant: 50 cubic centimeters nitric acid, 20 cubic centimeters water, 30 grams ammonium bifluoride. (Photographs show thickness dimension of specimens.)

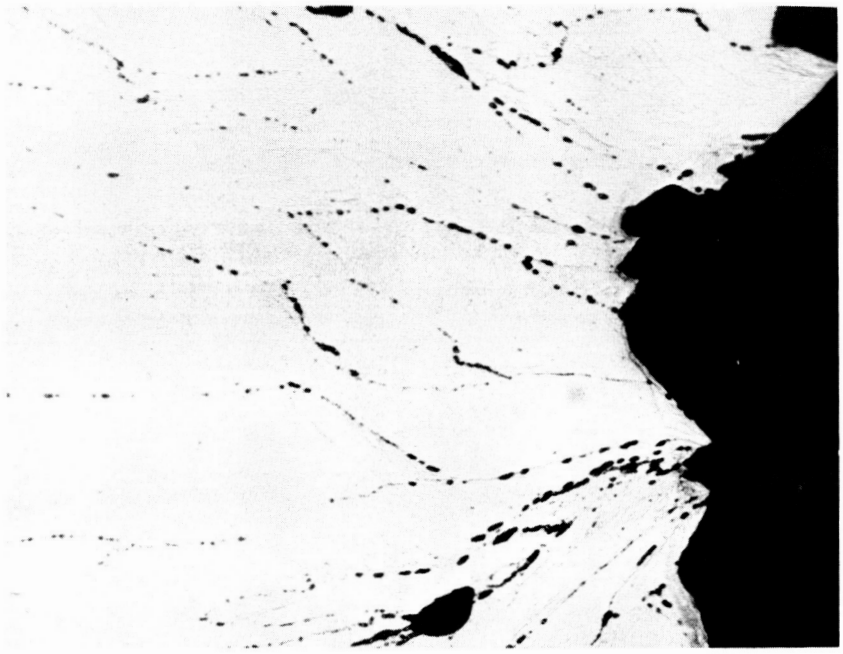


(e) 740 ppm nitrogen.

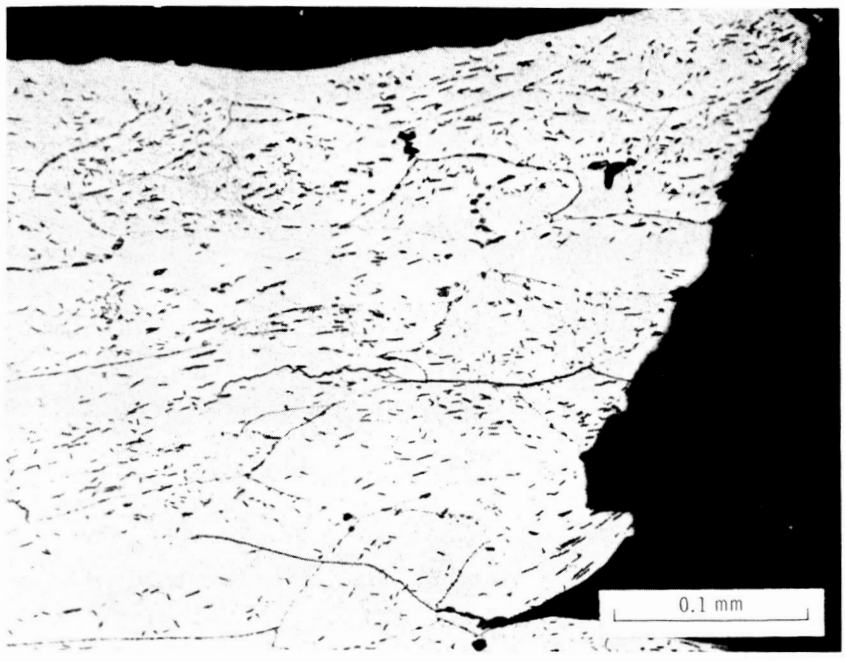


(f) 1225 ppm nitrogen.

Figure 9. - Concluded.

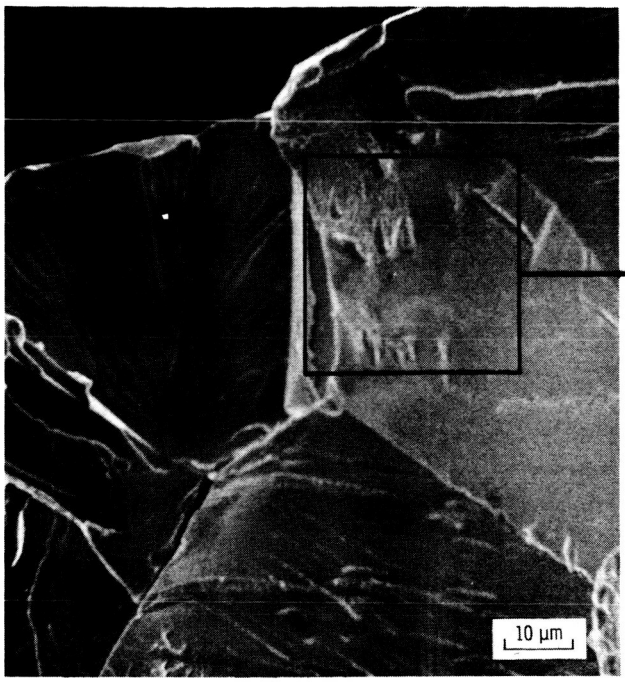


(a) 14 ppm nitrogen (typical fracture zone structure for specimens containing 14 to 505 ppm nitrogen).

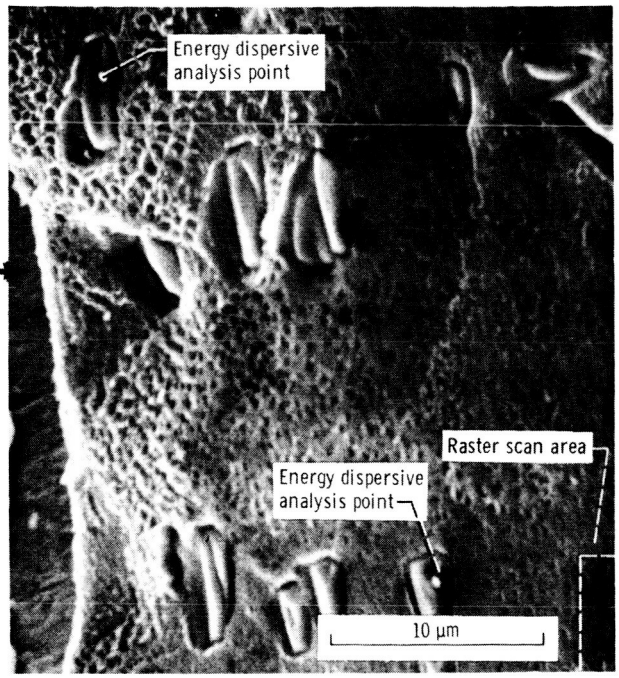


(b) 740 ppm nitrogen (typical fracture zone structure for specimens containing 740 to 1225 ppm nitrogen).

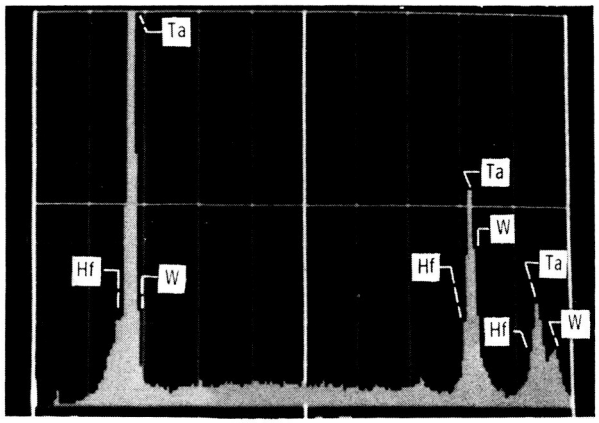
Figure 10. - Microstructures of test sections of nitrogen-doped-and-homogenized T-111 tubing specimens tensile tested at 900° C. Etchant: 50 cubic centimeters nitric acid, 20 cubic centimeters water, 30 grams ammonium bifluoride.



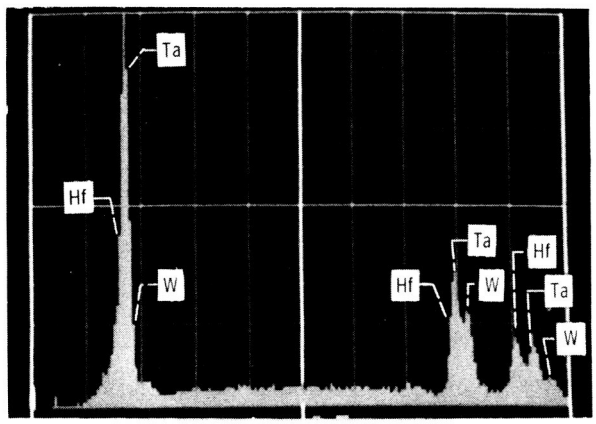
(a) Fracture surface.



(b) Possible grain boundary surface.



(c) Raster scan of matrix.



(d) Typical particle analysis.

Figure 11. - Scanning electron microscope analysis of fracture surface of T-111 specimen containing 1150 ppm nitrogen after tensile testing at 1200° C. (Refractured at room temperature to retain particles for examination.)

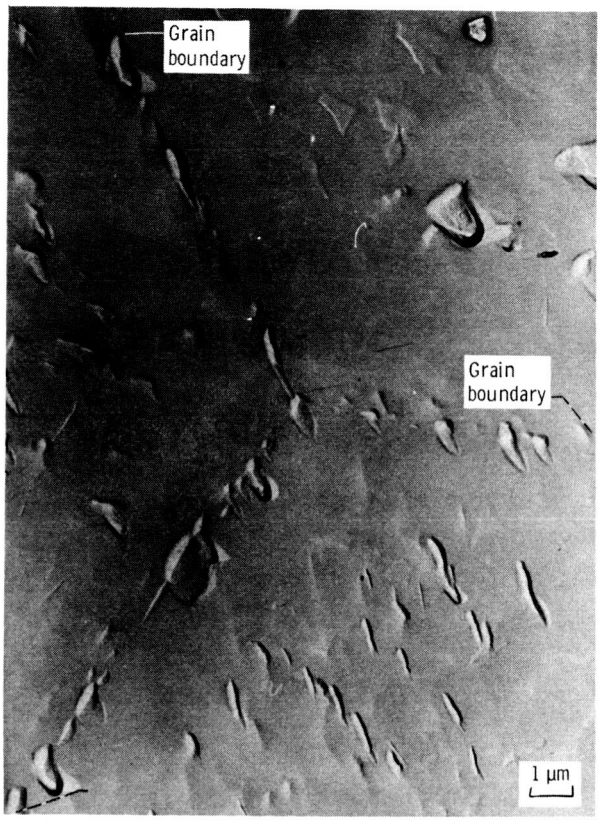


Figure 12. - Electron micrograph of carbon replica of T-111 specimen containing 439 ppm nitrogen and tensile tested at 760° C.

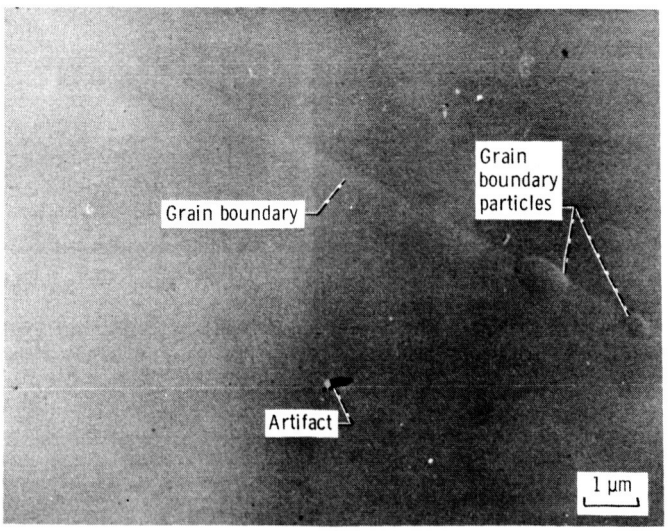


Figure 13. - Electron micrograph of carbon replica of T-111 specimen containing 14 ppm nitrogen and tensile tested at 760° C.

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